TechBrief

Liqui-Cel®
MEMBRANE CONTACTORS

# Using 'TransMembraneChemiSorption' (TMCS) for Ammonia Removal from Industrial Waste Waters

## Introduction

Dissolved gases like $NH_3$, $H_2S$ or NOx in waste water lead to contamination in the sewage system and high treatment costs for municipal waste water treatment plants. This translates into high penalty fees that are paid by the company discharging these contaminates into the sewage stream. In many cases a membrane-based water treatment system can be justified because of a favorable pay back time.

## Advantages

- Compact module design
- Single step In-line processing
- High quality usable outlet
- Low energy demand
- No air polution
- Up to 95% removal

Large-scale systems using conventional treatment processes such as extraction, stripping, or absorption can lead to several problems or issues. These issues may be overcome by using an alternate solution of Membrane Contactor technology. Membrane Contactors can remove ammonia from waste water and recover it to a usable form in a single step.

It is therefore an adequate and desirable solution for treating the ammonia waste water without polluting the air.

## Process description

Ammonium ion ($NH_4$+) in water reacts with hydroxide ion (OH-) according to the following **Equation 1**.

$$NH_4^+ + OH^- \leftrightarrow NH_3(g) + H_2O(l) \qquad \textbf{Eq 1}$$

This reaction is reversible and can be driven forward or backward depending on the water pH as shown in **Figure 1**.

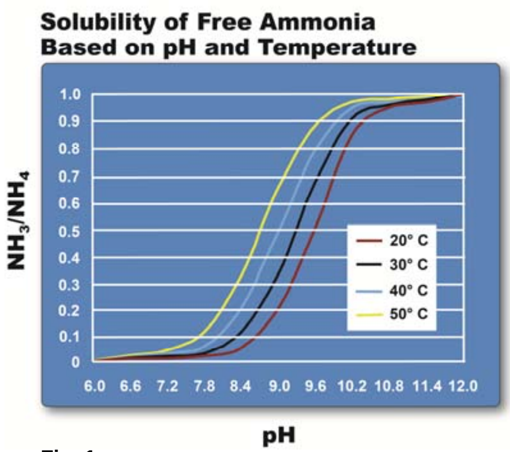


**Fig. 1**

At a pH of 11.3 or higher, the equilibrium favors the formation of free ammonia gas which can be removed from a waste water solution across the air filled pores of a microporous hydrophobic membrane when a proper driving force is maintained. The small pore size and the hydrophobic nature of membrane prevents the liquid phase from entering into the pores or flowing through the porous wall due to surface tension effects.

Because of the very low Henry constant and high solubility of $NH_3$ compared to other dissolved gases in water, such as $CO_2$ or $O_2$, the free ammonia gas will be difficult to remove by applying vacuum or by using a sweep gas-vacuum combination as in typical degassing operations with Membrane Contactor technology.

However, an acid solution will work very effectively as a means of removing the ammonia gas from waste water. The low-pH sulphuric acid solution will instantly react with ammonia gas according to **Equation 2** below to form ammonium sulphate. This will generate and maintain the concentration differential or driving force for removing ammonia from waste water.

$$2NH_3 + H_2SO_4 \leftrightarrow (NH_4)_2SO_4 \qquad \textbf{Eq 2}$$

The process above generates a concentrated solution of up to 30% of ammonia sulphate, which is a fertilizer.

This process, also described as: "TransMembrane-ChemiSorbtion" (TMCS), is shown schematically on a single fiber in **Figure 2**.

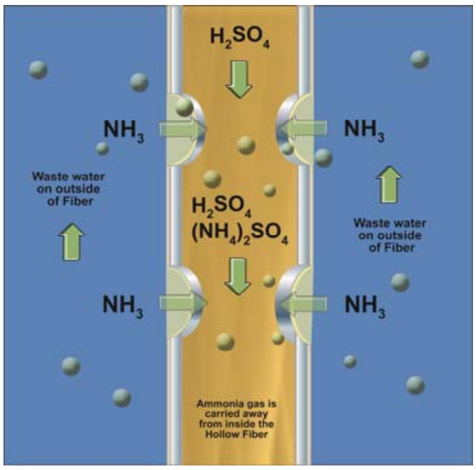


**Fig. 2: TMCS process scheme for ammonia removal**

The waste water flows through the shellside of the contactor (outside of the membrane), while an acid solution, such as sulphuric acid, circulates on the lumenside. (Figure 3 on following page shows the flow paths of both streams.)

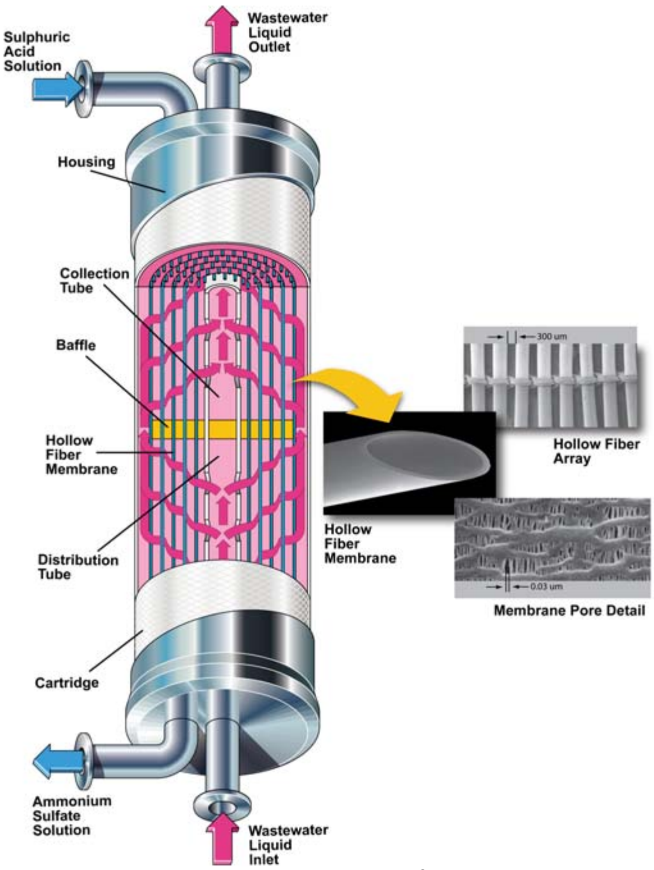


**Fig. 3: TMCS of ammonia using Liqui-Cel® Module**

## System design

In 2002 Membrana GmbH in Wuppertal Germany installed a TMCS pilot plant to test the removal of ammonia from waste water with the purpose of reducing waste water disposal costs at the manufacturing plant. In the first step, a system utilizing two 6x28 Liqui-Cel® Contactors (2x1 system configuration) with X-50 Hollow Fiber was installed to treat 0.5-1 m³/hr of waste water.

After it was determined that X-50 still provided superior ammonia stripping performance and successful trials on the 6-inch system, the plant was redesigned in 2004 to operate up to 30 m³/hr with a 2x1 system utilizing 14x28 Liqui-Cel Contactors with X-50 fiber.

The waste water stream consisted of two inlets with different $NH_3$ concentrations and temperatures so that different test cycles could be run. The different system sizes (6-inch and 14-inch) where fully adjustable so that configuration changes from 1x2 to a 2x1 system were possible. The general system design with two contactors in series is illustrated in **Figure 4.**

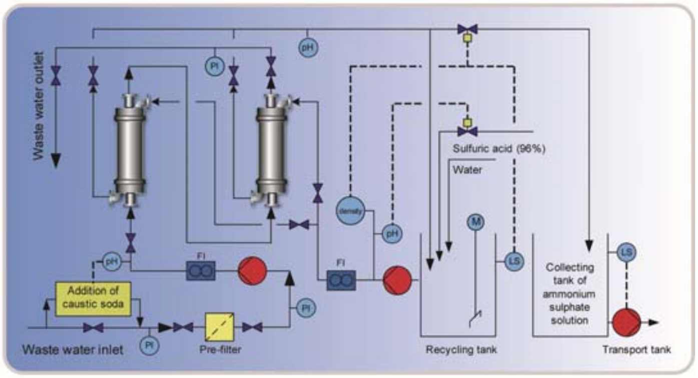


**Fig. 4: Basic P&ID of a TMCS system with two contactors in series**

The goal of the Liqui-Cel® Contactor TMCS system was to remove 90% of the ammonia at the Membrana GmbH plant site. The performance of the system has exceeded expectations with a removal rate of 95%.

### Ideal Process Parameters for Ammonia Removal

- $NH_3$ inlet conc. >500ppm
- Pre-filtration <10µm abs
- Temperature 40-55°C
- Feed stream pH>10
- Acid stream pH<2

The acid and caustic consumption depends on the inlet water, the pH, the water temperature and the ammonia content. When the inlet parameters are closest to being in the free ammonia state, with concentrations suitable for membrane contactor treatment that fit within the operating window of the TMCS process, less acid and caustic will be required.



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